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**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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**INVENTOR(S)**

Given Name (first and middle [if any])  Shihe Paul Joseph	Family Name or Surname  Xu Schalk	Residence (City and either State or Foreign Country)  Midland, Michigan 48640 Bay City, Michigan 48706
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Additional inventors are being named on the \_\_\_\_\_ separately numbered sheets attached hereto

**TITLE OF THE INVENTION (280 characters max)**

Organic Light-Emitting Diode

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**ENCLOSED APPLICATION PARTS (check all that apply)**

<input checked="" type="checkbox"/> Specification	Number of Pages <b>16</b>	<input type="checkbox"/> CD(s), Number _____
<input checked="" type="checkbox"/> Drawing(s)	Number of Sheets <b>1</b>	<input checked="" type="checkbox"/> Other (specify) Claims - 2 pages Abstract 1 page
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76		

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The invention was made by an agency of the United States Government or under a contract with an agency of the  
United States Government. No. Yes, the name of the U.S. Government agency and the Government contract number are: \_\_\_\_\_

Respectfully submitted,

SIGNATURE *Larry A. Milco*TYPED or PRINTED NAME **Larry A. Milco**TELEPHONE **989-496-3161**Date **3/16/04**

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**41,196**

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**DC10028PSP1****USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**

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UNITED STATES PATENT APPLICATION  
FOR  
[0001] ORGANIC LIGHT-EMITTING DIODE

FIELD OF THE INVENTION

[0002] The present invention relates to an organic light-emitting diode (OLED) and more particularly to an organic light-emitting diode containing a hole-transport layer comprising a cured polysiloxane prepared by applying an organosilicon composition to form a film and exposing the film to moisture, wherein the organosilicon composition comprises at least one silane having a group selected from carbazolyl, fluoroalkyl, and pentafluorophenylalkyl.

BACKGROUND OF THE INVENTION

[0003] Organic light-emitting diodes (OLEDs) are useful in a variety of consumer products, such as watches, telephones, lap-top computers, pagers, cellular phones, digital video cameras, DVD players, and calculators. Displays containing light-emitting diodes have numerous advantages over conventional liquid-crystal displays (LCDs). For example, OLED displays are thinner, consume less power, and are brighter than LCDs. Also, unlike LCDs, OLED displays are self-luminous and do not require backlighting. Furthermore, OLED displays have a wide viewing angle, even in bright light. As a result of these combined features, OLED displays are lighter in weight and take up less space than LCD displays.

[0004] OLEDs typically comprise a light-emitting element interposed between an anode and a cathode. The light-emitting element typically comprises a stack of thin organic layers comprising a hole-transport layer, an emissive layer, and an electron-transport layer.

However, OLEDs can also contain additional layers, such as a hole-injection layer and an electron-injection layer. Furthermore, the emissive layer can contain a fluorescent dye or dopant to enhance the electroluminescent efficiency of the OLED and control color output.

[0005] Although a variety of organic polymers can be used to prepare the hole-transport layer in an OLED, poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate), PDOT:PSS, is a preferred hole-transport material. OLEDs containing this material typically have a low turn-on voltage and high brightness. However, a hole-transport layer comprising PDOT:PSS has many limitations, including low transparency, high acidity, susceptibility to electrochemical de-doping (migration of dopant from hole-transport layer) and electrochemical

decomposition. Moreover, PDOT:PSS is insoluble in organic solvents and aqueous emulsions of the polymer, used to prepare the hole-transport layer, have limited stability. Consequently, there is a need for an OLED comprising a hole-transport layer that overcomes the aforementioned limitations.

### SUMMARY OF THE INVENTION

[0006] The present invention is directed to an organic light-emitting diode comprising:  
a substrate having a first opposing surface and a second opposing surface;  
a first electrode layer overlying the first opposing surface;  
a light-emitting element overlying the first electrode layer, the light-emitting element comprising  
a hole-transport layer and  
an emissive/electron-transport layer, wherein the hole-transport layer and the emissive/electron-transport layer lie directly on one another, and the hole-transport layer comprises a cured polysiloxane prepared by applying an organosilicon composition to form a film and exposing the film to moisture, wherein the organosilicon composition comprises (A) at least one silane having the formula  $R^1SiX_3$  and (B) an organic solvent, wherein each  $R^1$  is independently selected from  $-Y-Cz$ ,  $-(CH_2)_m-C_nF_{2n+1}$ , and  $-(CH_2)_m-C_6F_5$ , wherein  $Cz$  is N-carbazolyl,  $Y$  is a divalent organic group,  $m$  is an integer from 2 to 10,  $n$  is an integer from 1 to 3, and  $X$  is a hydrolysable group; and  
a second electrode layer overlying the light-emitting element.

[0007] The OLED of the present invention has a low turn-on voltage and high brightness. Also, the hole-transport layer of the present invention, which comprises a cured polysiloxane, exhibits high transparency and a neutral pH. Moreover, the silane in the organosilicon composition used to prepare the hole-transport layer is soluble in organic solvents, and the composition has good stability in the absence of moisture.

[0008] The organic light-emitting diode of the present invention is useful as a discrete light-emitting device or as the active element of light-emitting arrays or displays, such as flat panel displays. OLED displays are useful in a number of devices, including watches, telephones, lap-top computers, pagers, cellular phones, digital video cameras, DVD players, and calculators.

[0009] These and other features, aspects, and advantages of the present invention will become better understood with reference to the following description, appended claims, and accompanying drawings.

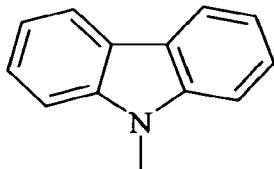
#### BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figure 1 shows a cross-sectional view of a first embodiment of an OLED according to the present invention.

[0011] Figure 2 shows a cross-sectional view of a second embodiment of an OLED according to the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

[0012] As used herein, the term “overlying” used in reference to the position of the first electrode layer, light-emitting element, and second electrode layer relative to the designated component means the particular layer either lies directly on the component or lies above the component with one or more intermediary layers there between, provided the OLED is oriented with the substrate below the first electrode layer as shown in Figures 1 and 2. For example, the term “overlying” used in reference to the position of the first electrode layer relative to the first opposing surface of the substrate in the OLED means the first electrode layer either lies directly on the surface or is separated from the surface by one or more intermediate layers. Further, the term “N-carbazolyl” refers to a group having the formula:



[0013] An organic light-emitting diode according to the present invention comprises:

- a substrate having a first opposing surface and a second opposing surface;
- a first electrode layer overlying the first opposing surface;
- a light-emitting element overlying the first electrode layer, the light-emitting element comprising
  - a hole-transport layer and

an emissive/electron-transport layer, wherein the hole-transport layer and the emissive/electron-transport layer lie directly on one another, and the hole-transport layer comprises a cured polysiloxane prepared by applying an organosilicon composition to form a film and exposing the film to moisture, wherein the organosilicon composition comprises (A) at least one silane having the formula  $R^1SiX_3$  and (B) an organic solvent, wherein each  $R^1$  is independently selected from -Y-Cz, -(CH<sub>2</sub>)<sub>m</sub>-C<sub>n</sub>F<sub>2n+1</sub>, and -(CH<sub>2</sub>)<sub>m</sub>-C<sub>6</sub>F<sub>5</sub>, wherein Cz is N-carbazolyl, Y is a divalent organic group, m is an integer from 2 to 10, n is an integer from 1 to 3, and X is a hydrolysable group; and a second electrode layer overlying the light-emitting element.

[0014] The substrate has a first opposing surface and a second opposing surface. Also, the substrate can be a rigid or flexible material. Further, the substrate can be transparent or nontransparent to light in the visible region of the electromagnetic spectrum. As used herein, the term "transparent" means the particular component (e.g., substrate or electrode layer) has a percent transmittance of at least 30%, alternatively at least 60%, alternatively at least 80%, for light in the visible region (~400 to ~700 nm) of the electromagnetic spectrum. Also, as used herein, the term "nontransparent" means the component has a percent transmittance less than 30% for light in the visible region of the electromagnetic spectrum.

[0015] Examples of substrates include, but are not limited to, semiconductor materials such as silicon, silicon having a surface layer of silicon dioxide, and gallium arsenide; quartz; fused quartz; aluminum oxide; ceramics; glass; metal foils; polyolefins such as polyethylene, polypropylene, polystyrene, and polyethyleneterephthalate; fluorocarbon polymers such as polytetrafluoroethylene and polyvinylfluoride; polyamides such as Nylon; polyimides; polyesters such as poly(methyl methacrylate) and poly(ethylene 2,6-naphthalenedicarboxylate); epoxy resins; polyethers; polycarbonates; polysulfones; and polyether sulfones.

[0016] The first electrode layer overlies the first opposing surface of the substrate. The first electrode layer can function as an anode or cathode in the OLED. The first electrode layer may be transparent or nontransparent to visible light. The anode is typically selected from a high work-function (> 4 eV) metal, alloy, or metal oxide such as indium oxide, tin oxide, zinc oxide, indium tin oxide (ITO), indium zinc oxide, aluminum-doped zinc oxide, nickel, and gold. The cathode can be a low work-function (< 4 eV) metal such as Ca, Mg, and Al; a high

work-function (> 4 eV) metal, alloy, or metal oxide, as described above; or an alloy of a low-work function metal and at least one other metal having a high or low work-function, such as Mg-Al, Ag-Mg, Al-Li, In-Mg, and Al-Ca. Methods of depositing anode and cathode layers in the fabrication of OLEDs, such as evaporation, co-evaporation, DC magnetron sputtering, or RF sputtering, are well known in the art.

[0017] The light-emitting element overlies the first electrode layer. The light-emitting element comprises a hole-transport layer and an emissive/electron-transport layer wherein the hole-transport layer and the emissive/electron-transport layer lie directly on one another, and the hole-transport layer comprises a cured polysiloxane, described below. The orientation of the light-emitting element depends on the relative positions of the anode and cathode in the OLED. The hole-transport layer is located between the anode and the emissive/electron-transport layer and the emissive/electron-transport layer is located between the hole-transport layer and the cathode. The thickness of the hole-transport layer is typically from 2 to 100 nm, alternatively from 10 to 70 nm, alternatively from 30 to 50 nm. The thickness of the emissive/electron-transport layer is typically from 20 to 100 nm, alternatively from 30 to 50 nm.

[0018] The hole-transport layer comprises a cured polysiloxane prepared by applying an organosilicon composition to form a film and exposing the film to moisture, wherein the organosilicon composition comprises (A) at least one silane having the formula  $R^1SiX_3$  and (B) an organic solvent, wherein each  $R^1$  is independently selected from -Y-Cz, -(CH<sub>2</sub>)<sub>m</sub>-C<sub>n</sub>F<sub>2n+1</sub>, and -(CH<sub>2</sub>)<sub>m</sub>-C<sub>6</sub>F<sub>5</sub>, wherein Cz is N-carbazolyl, Y is a divalent organic group, m is an integer from 2 to 10, n is an integer from 1 to 3, and X is a hydrolysable group. Alternatively, the subscript m is an integer from 2 to 7 or from 2 to 5. Also, alternatively, the subscript n is an integer from 1 to 2.

[0019] An organosilicon composition is applied to the first electrode layer, a layer overlying the first electrode layer, such as a hole-injection layer, or the emissive/electron-transport layer, depending on the configuration of the OLED, to form a film, wherein the organosilicon composition comprises components (A) and (B), described below.

[0020] Component (A) of the organosilicon composition is at least one silane having the formula  $R^1SiX_3$ , wherein each  $R^1$  is independently selected from -Y-Cz, -(CH<sub>2</sub>)<sub>m</sub>-

$C_nF_{2n+1}$ , and  $-(CH_2)_m-C_6F_5$ , wherein Cz is N-carbazolyl, Y is a divalent organic group, m is an integer from 2 to 10, n is an integer from 1 to 3, and X is a hydrolysable group.

[0021] The divalent organic groups represented by Y typically have from 1 to 10 carbon atoms, alternatively from 1 to 6 carbon atoms, alternatively from 1 to 4 carbon atoms. In addition to carbon and hydrogen, the divalent organic groups may contain other atoms such as nitrogen, oxygen, and halogen, provided the divalent group does not inhibit formation of the cured polysiloxane, described below. Examples of divalent organic groups represented by Y include, but are not limited to, C<sub>1</sub> to C<sub>10</sub> alkylene such as methylene, ethylene, propylene, butylenes, 2-methyl-1,3-propanediyl; halogen-substituted alkylene such as chloroethylene and fluoroethylene; alkyleneoxyalkylene such as  $-CH_2OCH_2CH_2CH_2-$ ,  $-CH_2CH_2OCH_2CH_2-$ ,  $-CH_2CH_2OCH(CH_3)CH_2-$ , and  $-CH_2OCH_2CH_2OCH_2CH_2-$ ; and carbonyloxyalkylene, such as  $-C(=O)O-(CH_2)_3-$ ; and phenylene.

[0022] Examples of carbazolyl groups represented by R<sup>1</sup> having the formula  $-Y-Cz$ , wherein Cz is N-carbazolyl and Y is a divalent organic group, include, but are not limited to, groups having the formulae:  $-CH_2-CH_2-Cz$ ,  $-(CH_2)_3-Cz$ ,  $-(CH_2)_4-Cz$ ,  $-(CH_2)_6-Cz$ , and  $-(CH_2)_8-Cz$ .

[0023] Examples of fluoroalkyl groups represented by R<sup>1</sup> having the formula  $-(CH_2)_m-C_nF_{2n+1}$ , wherein m and n are as defined and exemplified above, include, but are not limited to, groups having the formulae:  $-CH_2-CH_2-CF_3$ ,  $-(CH_2)_3-CF_3$ ,  $-(CH_2)_4-C_2F_5$ ,  $-(CH_2)_6C_3F_7$ , and  $-(CH_2)_8-CF_3$ .

[0024] Examples of pentafluorophenylalkyl groups represented by R<sup>1</sup> having the formula  $-(CH_2)_m-C_6F_5$ , wherein m is as defined and exemplified above, include, but are not limited to, groups having the formulae:  $-CH_2-CH_2-C_6F_5$ ,  $-(CH_2)_3-C_6F_5$ ,  $-(CH_2)_4-C_6F_5$ ,  $-(CH_2)_6-C_6F_5$ , and  $-(CH_2)_8-C_6F_5$ .

[0025] As used herein, the term "hydrolysable group" means the silicon-bonded group X can react with water to form a silicon-bonded -OH (silanol) group. Examples of hydrolysable groups represented by X include, but are not limited to, -Cl, -Br, -OR<sup>2</sup>, -OCH<sub>2</sub>CH<sub>2</sub>OR<sup>2</sup>, CH<sub>3</sub>C(=O)O-, Et(Me)C=N-O-, CH<sub>3</sub>C(=O)N(CH<sub>3</sub>)-, and -ONH<sub>2</sub>, wherein R<sup>2</sup> is hydrocarbyl or halogen-substituted hydrocarbyl.

[0026] The hydrocarbyl and halogen-substituted hydrocarbyl groups represented by R<sup>2</sup> typically have from 1 to 8 carbon atoms, alternatively from 3 to 6 carbon atoms. Acyclic hydrocarbyl and halogen-substituted hydrocarbyl groups containing at least 3 carbon atoms can have a branched or unbranched structure. Examples of hydrocarbyl groups include, but are not limited to, unbranched and branched alkyl, such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 1-ethylpropyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, hexyl, heptyl, and octyl; cycloalkyl, such as cyclopentyl, cyclohexyl, and methylcyclohexyl; phenyl; alkaryl, such as tolyl and xylyl; aralkyl, such as benzyl and phenethyl; alkenyl, such as vinyl, allyl, and propenyl; arylalkenyl, such as styryl; and alkynyl, such as ethynyl and propynyl. Examples of halogen-substituted hydrocarbyl groups include, but are not limited to, 3,3,3-trifluoropropyl, 3-chloropropyl, chlorophenyl, and dichlorophenyl.

[0027] Examples of silanes include, but are not limited to, carbazolyl-substituted silanes such as CzCH<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>, CzCH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub>, Cz(CH<sub>2</sub>)<sub>3</sub>SiCl<sub>3</sub>, Cz(CH<sub>2</sub>)<sub>4</sub>SiCl<sub>3</sub>, Cz(CH<sub>2</sub>)<sub>6</sub>SiCl<sub>3</sub>, and Cz(CH<sub>2</sub>)<sub>8</sub>SiCl<sub>3</sub>, wherein Cz is N-carabazolyl; fluoroalkyl-substituted silanes include such as CF<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>SiCl<sub>3</sub>, CF<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>SiCl<sub>3</sub>, CF<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>SiCl<sub>3</sub>, CF<sub>3</sub>CF<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>SiCl<sub>3</sub>, CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub>, CF<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>Si(OAc)<sub>3</sub>, and CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>3</sub>, wherein OAc is acetoxy; and pentafluorophenylalkyl-substituted silanes such as C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>, C<sub>6</sub>F<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub>,

[0028] Component (A) can be a single silane or a mixture comprising two or more different silanes, each having the formula R<sup>1</sup>SiX<sub>3</sub>, wherein R<sup>1</sup> and X are as defined and exemplified above.

[0029] The concentration of component (A) is typically from 0.01 to 20% (w/w), alternatively from 0.5 to 10% (w/w), alternatively from 2 to 7% (w/w), based on the total weight of the organosilicon composition.

[0030] Methods of preparing fluoroalkyl- and pentafluorophenylalkyl-substituted silanes are well known in the art; many of these silanes are commercially available. Carbazolyl-substituted silanes can be prepared by reacting an N-alkenyl carbazole, for example allyl carbazole, with a trifunctional silane, such as trichlorosilane, in the presence of a platinum catalyst, as described in Example 1 below.

[0031] Component (B) of the silicone composition is at least one organic solvent. The organic solvent can be any nonpolar aprotic or dipolar aprotic organic solvent that does not react with the silane (component (A)), or other components of the composition, and is miscible with the silane. The organic solvent typically has a normal boiling point of from 80 to 200 °C, alternatively from 90 to 150 °C.

[0032] Examples of organic solvents include, but are not limited to, aromatic hydrocarbons such as benzene, toluene, xylene and mesitylene; cyclic ethers such as tetrahydrofuran (THF) and dioxane; ketones such as methyl isobutyl ketone (MIBK), cyclopentanone, and cyclohexanone; halogenated alkanes such as trichloroethane; and halogenated aromatic hydrocarbons such as bromobenzene and chlorobenzene. Component (B) can be a single organic solvent or a mixture comprising two or more different organic solvents, each as defined above.

[0033] The concentration of component (B) is typically from 80 to 99.99% (w/w), alternatively from 90 to 99.5% (w/w), alternatively from 93 to 98% (w/w), based on the total weight of the organosilicon composition.

[0034] The organosilicon composition can further comprise at least one cross-linking agent having the formula  $R^2_pSiX_{4-p}$ , wherein  $R^2$  and X are as described above for the silane and p is 0 or 1. Examples of cross-linking agents include, but are not limited to, chlorosilanes such as  $SiCl_4$ ,  $CH_3SiCl_3$ ,  $CH_3CH_2SiCl_3$ , and  $C_6H_5SiCl_3$ ; bromosilanes such as  $SiBr_4$ ,  $CH_3SiBr_3$ ,  $CH_3CH_2SiBr_3$ , and  $C_6H_5SiBr_3$ ; alkoxy silanes such as  $CH_3Si(OCH_3)_3$ ,  $CH_3Si(OCH_2CH_3)_3$ ,  $CH_3Si(OCH_2CH_2CH_3)_3$ ,  $CH_3Si[O(CH_2)_3CH_3]_3$ ,  $CH_3CH_2Si(OCH_2CH_3)_3$ ,  $C_6H_5Si(OCH_3)_3$ ,  $C_6H_5CH_2Si(OCH_3)_3$ ,  $C_6H_5Si(OCH_2CH_3)_3$ ,  $CH_2=CHSi(OCH_3)_3$ ,  $CH_2=CHCH_2Si(OCH_3)_3$ ,  $CF_3CH_2CH_2Si(OCH_3)_3$ ,  $CH_3Si(OCH_2CH_2OCH_3)_3$ ,  $CF_3CH_2CH_2Si(OCH_2CH_2OCH_3)_3$ ,  $CH_2=CHSi(OCH_2CH_2OCH_3)_3$ ,  $CH_2=CHCH_2Si(OCH_2CH_2OCH_3)_3$ ,  $C_6H_5Si(OCH_2CH_2OCH_3)_3$ ,  $Si(OCH_3)_4$ ,  $Si(OC_2H_5)_4$ , and  $Si(OC_3H_7)_4$ ; organoacetoxysilanes such as  $CH_3Si(OAc)_3$ ,  $CH_3CH_2Si(OAc)_3$ ,  $CH_2=CHSi(OAc)_3$ , and  $Si(OAc)_4$ ; organoiminooxysilanes such as  $CH_3Si[O-N=C(CH_3)CH_2CH_3]_3$ ,  $Si[O-N=C(CH_3)CH_2CH_3]_4$ , and  $CH_2=CHSi[O-N=C(CH_3)CH_2CH_3]_3$ ; organoacetamidosilanes

such as  $\text{CH}_3\text{Si}[\text{NHC}(=\text{O})\text{CH}_3]_3$  and  $\text{C}_6\text{H}_5\text{Si}[\text{NHC}(=\text{O})\text{CH}_3]_3$ ; amino silanes such as  $\text{CH}_3\text{Si}[\text{NH}(\text{s-C}_4\text{H}_9)]_3$  and  $\text{CH}_3\text{Si}(\text{NHC}_6\text{H}_{11})_3$ ; and organoaminoxy silanes.

[0035] The cross-linking agent can be a single crosslinking agent or a mixture comprising two or more different cross-linking agents, each as described above. Also, methods of preparing tri- and tetra-functional silanes are well known in the art; many of these silanes are commercially available.

[0036] The concentration of the cross-linking agent in the organosilicon composition is typically sufficient to provide up to 60 mol% of silicon-bonded hydrolysable groups, alternatively up to 25 mol% of silicon-bonded hydrolysable groups, based on the total number of moles of the silane, component (A). The optimum amount of the cross-linking agent can be readily determined by routine experimentation.

[0037] The reaction mixture can further comprise at least one hydrolysis catalyst. The hydrolysis catalyst can be any acid catalyst or basic catalyst typically used to catalyze the hydrolysis of organosilanes containing hydrolysable groups that do not react with water to form an acid or a base.

[0038] Examples of acid catalysts include, but are not limited to, inorganic acids such as hydrochloric acid, sulfuric acid, nitric acid, and hydrofluoric acid; and organic acids such as acetic acid, oxalic acid, and trifluoroacetic acid. The acid catalyst can be a single acid catalyst or a mixture comprising two or more different acid catalysts.

[0039] Examples of alkali catalysts include, but are not limited to, inorganic bases such as ammonium hydroxide; and organic bases such as tetramethylammonium hydroxide, tetrabutylammonium hydroxide, and tetrabutylphosphonium hydroxide. The alkali catalyst can be a single alkali catalyst or a mixture comprising two or more different alkali catalysts.

[0040] When used, the concentration of the hydrolysis catalyst is sufficient to catalyze the hydrolysis of the hydrolysable group X in the silane, component (A). For example, the concentration of the hydrolysis catalyst is typically from 0.1 to 10% (w/w), alternatively from 0.1 to 3% (w/w), alternatively from 0.1 to 1% (w/w), based on the total weight of the organosilicon composition.

[0041] The organosilicon composition of the instant invention is typically prepared by combining components (A) and (B) and any optional ingredients in the stated proportions at ambient temperature. Mixing can be accomplished by any of the techniques known in the art such as milling, blending, and stirring, either in a batch or continuous process. The particular

device is determined by the viscosity of the components and the viscosity of the final silicone composition.

[0042] The organosilicon composition can be applied to the first electrode layer, a layer overlying the first electrode layer, such as a hole-injection layer, or the emissive/electron-transport layer, depending on the configuration of the OLED, to form a film, using conventional methods such as spin-coating, dipping, spraying, brushing, and printing.

[0043] The film is exposed to moisture to form the cured polysiloxane. Formation of the cured polysiloxane can be accelerated by application of heat and/or exposure to high humidity. The rate of formation of the cured polysiloxane depends on a number of factors, including temperature, humidity, structure of the silane, and nature of the hydrolysable groups. For example, the cured polysiloxane is typically formed by exposing the film to a relative humidity of about 30% at a temperature of from about room temperature (23 °C) to about 150 °C, for period from 0.5 to 72 h.

[0044] The emissive/electron-transport layer can be any low molecular weight organic compound or organic polymer typically used as an emissive, electron-transport, electron-injection/electron-transport, or light-emitting material in OLED devices. Low molecular weight organic compounds suitable for use as the electron-transport layer are well known in the art, as exemplified in U.S. Patent No. 5,952,778; U.S. Patent No. 4,539,507; U.S. Patent No. 4,356,429; U.S. Patent No. 4,769,292; U.S. Patent No. 6,048,573; and U.S. Patent No. 5,969,474. Examples of low molecular weight compounds include, but are not limited to, aromatic compounds, such as anthracene, naphthalene, phenanthrene, pyrene, chrysene, and perylene; butadienes such as 1,4-diphenylbutadiene and tetraphenylbutadiene; coumarins; acridine; stilbenes such as trans-stilbene; and chelated oxinoid compounds, such as tris(8-hydroxyquinolato)aluminum(III), Alq<sub>3</sub>. These low molecular weight organic compounds may be deposited by standard thin-film preparation techniques including vacuum evaporation and sublimation.

[0045] Organic polymers suitable for use as the emissive/electron-transport layer are well known in the art, as exemplified in U.S. Patent No. 5,952,778; U.S. Patent No. 5,247,190; U.S. Patent No. 5,807,627; U.S. Patent No. 6,048,573; and U.S. Patent No. 6,255,774. Examples of organic polymers include, but are not limited to, poly(phenylene vinylene)s, such as poly(1,4 phenylene vinylene); poly-(2,5-dialkoxy-1,4 phenylene vinylene)s, such as poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEHPPV), poly(2-methoxy-

5-(2-methylpentyloxy)-1,4-phenylenevinylene), poly(2-methoxy-5-pentyloxy-1,4-phenylenevinylene), and poly(2-methoxy-5-dodecyloxy-1,4-phenylenevinylene); poly(2,5-dialkyl-1,4 phenylene vinylene)s; poly(phenylene); poly(2,5-dialkyl-1,4 phenylene)s; poly(p-phenylene); poly(thiophene)s, such as poly(3-alkylthiophene)s; poly(alkylthienylene)s, such as poly(3-dodecylthienylene); poly(fluorene)s, such as poly(9,9-dialkyl fluorine)s; and polyanilines. Examples of organic polymers also include the polyfluorene-based light-emitting polymers available from The Dow Chemical Company (Midland, MI), under the trademark LUMATION, such as LUMATION Red 1100 Series Light-Emitting Polymer, LUMATION Green 1300 Series Light-Emitting Polymer, and LUMATION Blue BP79 Light Emitting Polymer. The organic polymers can be applied by conventional solvent coating techniques such as spin-coating, dipping, spraying, brushing, and printing (e.g., stencil printing and screen printing).

[0046] The emissive/electron-transport layer can further comprise a fluorescent dye. Fluorescent dyes suitable for use in OLED devices are well known in the art, as illustrated in U.S. Patent No. 4,769,292. Examples of fluorescent dyes include, but are not limited to, coumarins; dicyanomethylenepyrans, such as 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)4H-pyran; dicyanomethylenethiopyrans; polymethine; oxabenzanthracene; xanthene; pyrylium and thiapyrylium; cabostyryl; and perylene fluorescent dyes.

[0047] The second electrode layer can function either as an anode or cathode in the OLED. The second electrode layer may be transparent or nontransparent to light in the visible region. Examples of anode and cathode materials and methods for their formation are as described above for the first electrode layer.

[0048] The OLED of the present invention can further comprise a hole-injection layer interposed between the anode and the hole-transport layer, and/or an electron-injection layer interposed between the cathode and the emissive/electron-transport layer. The hole-injection layer typically has a thickness of from 1 to 20 nm, alternatively from 7 to 10 nm. Examples of materials suitable for use as the hole-injection layer include, but are not limited to, copper phthalocyanine. The electron-injection layer typically has a thickness of from 0.5 to 5 nm, alternatively from 1 to 3 nm. Examples of materials suitable for use as the electron-injection layer include, but are not limited to, alkali metal fluorides, such as lithium fluoride and cesium fluoride; and alkali metal carboxylates, such as lithium acetate and cesium acetate.

The hole-injection layer and the hole-injection layer can be formed by conventional techniques, thermal evaporation.

[0049] As shown in Figure 1, a first embodiment of an OLED according to the present invention comprises a substrate **100** having a first opposing surface **100A** and a second opposing surface **100B**, a first electrode layer **102** overlying the first opposing surface **100A**, wherein the first electrode layer **102** is an anode, a light-emitting element **104** overlying the first electrode layer **102**, wherein the light-emitting element **104** comprises a hole-transport layer **106** and an emissive/electron-transport layer **108** lying directly on the hole-transport layer **106**, wherein the hole-transport layer **106** comprises a cured polysiloxane, and a second electrode layer **110** overlying the light-emitting element **104**, wherein the second electrode layer **110** is a cathode.

[0050] As shown in Figure 2, a second embodiment of an OLED according to the present invention comprises a substrate **200** having a first opposing surface **200A** and a second opposing surface **200B**, a first electrode layer **202** overlying the first opposing surface **200A**, wherein the first electrode layer **202** is a cathode, a light-emitting element **204** overlying the first electrode layer **202**, wherein the light-emitting element **204** comprises an emissive/electron-transport layer **208** and a hole-transport layer **206** lying directly on the emissive/electron-transport layer **208**, wherein the hole-transport layer **206** comprises a cured polysiloxane, and a second electrode layer **210** overlying the light-emitting element **204**, wherein the second electrode layer **210** is an anode.

[0051] The OLED of the present invention has a low turn-on voltage and high brightness. Also, the hole-transport layer of the present invention, which comprises a cured polysiloxane, exhibits high transparency and a neutral pH. Moreover, the silane in the organosilicon composition used to prepare the hole-transport layer is soluble in organic solvents, and the composition has good stability in the absence of moisture.

[0052] The organic light-emitting diode of the present invention is useful as a discrete light-emitting device or as the active element of light-emitting arrays or displays, such as flat panel displays. OLED displays are useful in a number of devices, including watches, telephones, lap-top computers, pagers, cellular phones, digital video cameras, DVD players, and calculators.

## EXAMPLES

[0053] The following examples are presented to better illustrate the OLED of the invention, but are not to be considered as limiting the invention, which is delineated in the appended claims. Unless otherwise noted, all parts and percentages reported in the examples are by weight. The following methods and materials were employed in the examples:

### Method of Cleaning ITO-Coated Glass Substrates

[0054] ITO-coated glass slides (Merck Display Technology, Inc., Taipei, Taiwan) having a surface resistance of 30 Ω/square were cut into 25-mm square substrates. The substrates were immersed in an ultrasonic bath containing a solution consisting of 1% Alconox powdered cleaner (Alconox, Inc.) in water for 10 min and then rinsed with deionized water. The substrates were then immersed sequentially in the each of the following solvents with ultrasonic agitation for 10 min in each solvent: isopropyl alcohol, n-hexane, and toluene. The glass substrates were then dried under a stream of dry nitrogen. Immediately prior to use, the substrates were treated with oxygen plasma for 3 min.

### Deposition of SiO in OLEDs

[0055] Silicon monoxide (SiO) was deposited by thermal evaporation using a BOC Edwards Auto 306 high vacuum deposition system equipped with a crystal balance film thickness monitor. The substrate was placed in a rotary sample holder positioned above the source and covered with the appropriate mask. The source was prepared by placing a sample of SiO in an aluminum oxide crucible. The crucible was then positioned in a tungsten wire spiral. The pressure in the vacuum chamber was reduced to  $2.0 \times 10^{-6}$  mbar. The substrate was allowed to outgas for at least 30 min at this pressure. The SiO film was deposited by heating the source via the tungsten filament while rotating the sample holder. The deposition rate (0.1 to 0.3 nm per second) and the thickness of the film were monitored during the deposition process.

### Deposition of LiF, Ca, and Al Films in OLEDs

[0056] Lithium fluoride, calcium, and aluminum films were deposited by thermal evaporation under an initial vacuum of  $10^{-6}$  mbar using a BOC Edwards model E306A Coating System equipped with a crystal balance film thickness monitor. The source was

prepared by placing the metal in an aluminum oxide crucible and positioning the crucible in a tungsten wire spiral, or by placing the metal directly in a tungsten basket. When multiple layers of different metals were required, the appropriate sources were placed in a turret that could be rotated for deposition of each metal. The deposition rate (0.1 to 0.3 nm per second) and the thickness of the film were monitored during the deposition process.

**[0057]** LUMATION Blue BP79 Light Emitting Polymer, available from The Dow Chemical Company (Midland, MI), is a polyfluorene polymer that emits light in the blue region of the visible spectrum.

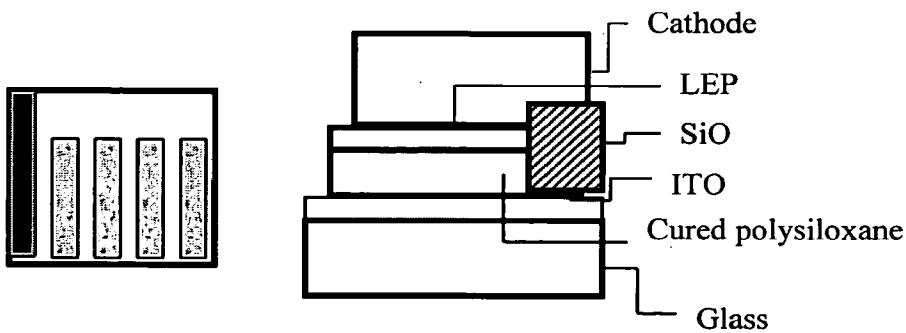
#### Example 1

**[0058]** Trichlorosilane (4.47 g), 5.52 g of allyl carbazole, and 5.5 g of anhydrous toluene were combined under nitrogen in a one-neck glass flask equipped with a magnetic stir bar. To the mixture was added 0.015 g of a solution consisting of 0.31% of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane and 0.19% of a platinum complex of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane in dry toluene. The mixture was heated under nitrogen at 60 °C for 1 h and then flushed with dry nitrogen at 60 °C for 10 min. The mixture was then distilled at about 220 °C under vacuum to produce 3-(*N*-carbazolyl)propyltrichlorosilane) as a colorless fluid, which formed transparent colorless crystals upon cooling to room temperature.

**[0059]** A portion (0.5 g) of the 3-(*N*-carbazolyl)propyltrichlorosilane) was dissolved in 9.5 g of toluene in a glass vial. A drop of the solution was applied to double-polished silicon wafer and the solvent was evaporated under a stream of dry nitrogen to form a thin film (4 µm). The FTIR spectrum of the film showed absorptions characteristic of the carbazole ring at 1598, 1484, 1452, 750 and 722 cm<sup>-1</sup>, Si-Cl absorptions at 564, 589, and 696 cm<sup>-1</sup>. No Si-OH or Si-O-Si absorptions were observed. The film was exposed to ambient air (30%RH) for 0.5 h, after which the Si-Cl absorptions were nearly absent, and a broad Si-O-S absorption centered at 1050 cm<sup>-1</sup> and a broad SiOH absorption centered at 3400 cm<sup>-1</sup> were observed. The film was heated at 100 °C for 60 min, after which a weak SiOH absorption was observed in the FTIR spectrum.

**Example 2**

[0060] Four OLEDs (see figures below) were fabricated as follows: Silicon monoxide (100 nm) was thermally deposited along a first edge of a pre-cleaned ITO-coated glass substrate (25 mm x 25 mm) through a mask having a rectangular aperture (6 mm x 25 mm). A strip of 3M Scotch brand tape (5mm x 25mm) was applied along a second edge of the substrate, perpendicular to the SiO deposit. A solution consisting of 4% of 3-(*N*-carbazolyl)propyltrichlorosilane and 1% of tetrachlorosilane in toluene was spin-coated (4,200 rpm, 20 s) over the ITO surface using a CHEMAT Technology Model KW-4A spin-coater to form a hole-transport layer having a thickness of 40 nm. The composite was exposed to the ambient air (30% RH) for 30 minutes, heated in an oven (air) at 100 °C for 90 min, and then allowed to cool to room temperature. A solution consisting of 1.5 wt % of LUMATION Blue BP79 Light-Emitting Polymer in mesitylene was then spin-coated (2250 rpm, 40 second) over the hole-transport layer to form an emissive/electron-transport layer having a thickness of 50 nm. The composite was heated in an oven under nitrogen at 100 °C for 30 min and then allowed to cool to room temperature. The strip of tape was removed from the substrate to expose the anode (ITO) and four cathodes were formed by depositing lithium fluoride (1 nm), calcium (50 nm) and aluminum (150 nm) sequentially on top of the light-emitting polymer layer and SiO deposit through a mask having four rectangular apertures (3 mm x 16 mm). Each of the four OLEDs emitted a blue color light and had a turn-on voltage at 1 cd m<sup>-2</sup> of about 2.8 V, a brightness at 7 V of approximately 6500 cd m<sup>-2</sup>, and a peak luminous efficiency of 6.7 cd A<sup>-1</sup>.



Overview

Cross-Section

**Example 3**

**[0061]** Four OLEDs were fabricated as described in Example 2, except the hole-transport layer was prepared using a solution consisting of 5% of 3-(pentafluorophenyl)propyltrichlorosilane in toluene. Also, the hole-transport layer was spin-washed with mesitylene (4200 rpm, 20 s) prior to formation of the emissive/electron transport layer. Each of the four OLEDs emitted a blue color light and had a turn-on voltage at 1 cd m<sup>-2</sup> of about 2.8 V, a brightness at 7 V of approximately 7700 cd m<sup>-2</sup>, and a peak luminous efficiency of 3.4 cd A<sup>-1</sup>.

**Example 4**

**[0062]** Four OLEDs were fabricated as described in Example 3, except the hole-transport layer was prepared using a solution consisting of 5% of 3,3,3-trifluoropropyltrichlorosilane in toluene. Each of the four OLEDs emitted a blue color light and had a turn-on voltage at 1 cd m<sup>-2</sup> of about 3.1 V, a brightness at 10 V of approximately 11700 cd m<sup>-2</sup>, and a peak luminous efficiency of 4.7 cd A<sup>-1</sup>.

That which is claimed is:

1. An organic light-emitting diode comprising:  
a substrate having a first opposing surface and a second opposing surface;  
a first electrode layer overlying the first opposing surface;  
a light-emitting element overlying the first electrode layer, the light-emitting element comprising  
a hole-transport layer and  
an emissive/electron-transport layer, wherein the hole-transport layer and the emissive/electron-transport layer lie directly on one another, and the hole-transport layer comprises a cured polysiloxane prepared by applying an organosilicon composition to form a film and exposing the film to moisture, wherein the organosilicon composition comprises (A) at least one silane having the formula  $R^1SiX_3$  and (B) an organic solvent, wherein each  $R^1$  is independently selected from -Y-Cz, -(CH<sub>2</sub>)<sub>m</sub>-C<sub>n</sub>F<sub>2n+1</sub>, and -(CH<sub>2</sub>)<sub>m</sub>-C<sub>6</sub>F<sub>5</sub>, wherein Cz is N-carbazolyl, Y is a divalent organic group, m is an integer from 2 to 10, n is an integer from 1 to 3, and X is a hydrolysable group; and  
a second electrode layer overlying the light-emitting element.
2. The organic light-emitting diode according to claim 1, wherein X in component (A) is -Cl or -Br.
3. The organic light-emitting diode according to claim 1, wherein R<sup>1</sup> in component (A) is -Y-Cz, wherein Cz is N-carbazolyl and Y is a divalent organic group.
4. The organic light-emitting diode according to claim 3, wherein Y is C<sub>1</sub> to C<sub>10</sub> alkylene.
5. The organic light-emitting diode according to claim 1, wherein R<sup>1</sup> in component (A) is -(CH<sub>2</sub>)<sub>m</sub>-C<sub>n</sub>F<sub>2n+1</sub> or -(CH<sub>2</sub>)<sub>m</sub>-C<sub>6</sub>F<sub>5</sub>, wherein m is an integer from 2 to 10 and n is an integer from 1 to 3.

6. The organic light-emitting diode according to claim 1, wherein the concentration of component (A) is from 0.5 to 10% (w/w), based on the total weight of the organosilicon composition.

7. The organic light-emitting diode according to claims 1, 3, or 5, wherein the organosilicon composition further comprises at least one cross-linking agent having the formula  $R^2_pSiX_{4-p}$ , wherein  $R^2$  is C<sub>1</sub> to C<sub>8</sub> hydrocarbyl or halogenated hydrocarbyl, X is a hydrolysable group, and p is 0 or 1.

8. The organic light-emitting diode according to claim 1, wherein the organosilicon composition further comprises at least one hydrolysis catalyst.

9. The organic light-emitting diode according to claim 1, wherein the emissive/electron transport layer comprises a fluorescent dye.

10. The organic light-emitting diode according to claim 1, further comprising at least one of a hole-injection layer and an electron injection layer.

## ABSTRACT

An organic light-emitting diode comprising a substrate having a first opposing surface and a second opposing surface; a first electrode layer overlying the first opposing surface; a light-emitting element overlying the first electrode layer, the light-emitting element comprising a hole-transport layer and an emissive/electron-transport layer, wherein the hole-transport layer and the emissive/electron-transport layer lie directly on one another, and the hole-transport layer comprises a cured polysiloxane prepared by applying an organosilicon composition to form a film and exposing the film to moisture to form the cured polysiloxane, wherein the organosilicon composition comprises at least one silane having a group selected from carbazolyl, fluoroalkyl, and pentafluorophenylalkyl; and a second electrode layer overlying the light-emitting element.

Figure 1

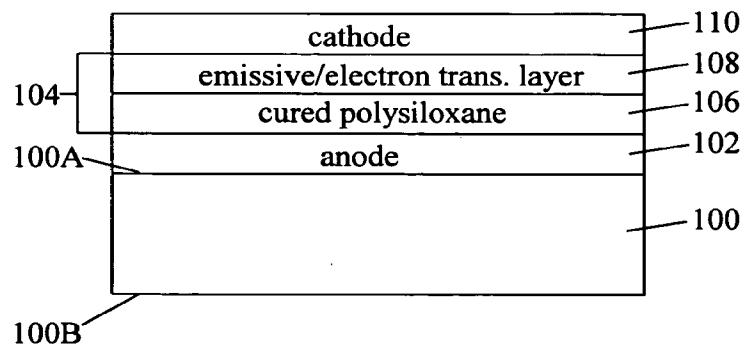


Figure 2

